Atmospheric Polycyclic Aromatic Hydrocarbons (Pahs) Concentration and Related Carcinogenic Potencies in the North Central Part of India

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Abstract **- Polycyclic Aromatic Hydrocarbons (PAHs) are chemicals containing two or more fused benzene rings in a linear, angular or cluster arrangement. PAH contain only carbon and hydrogen. They belong to the group of persistent organic pollutants (POPs) know for their chemical carcinogenicity. They are released into the environment from anthropogenic sources such as combustion of fossil fuels, refused burning; industrial process and motor vehicle exhaust which results in occurrence of PAH in many parts of environment. Atmospheric particulate matter from four different areas within Agra city (a semi-arid region) was collected using respirable dust samplers was then extracted with dichloromethane using an automated Soxhlet Extraction System (Soxtherm®). The extracts were analyzed for 17 target Polycyclic Aromatic Hydrocarbons (PAHs). The total PAH (TPAH) concentrations were 76.6, 27.9, 23.7 and 6.5 nanograms per cubic meter (ng m^{-3}), respectively, at the industrial, residential, roadside and agricultural sites. The combined mean concentration of TPAH was 33.7 ng m^{-3} for all sites. The industrial site had the highest TPAH concentration followed in order by the residential, roadside and agricultural sites. Indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene and benzo(b)fluoranthene were the predominant compounds found in the samples collected from all of the sites. The average B(a)P-equivalent exposure, calculated by using toxic equivalent factors (TEFs) derived from literature and the USEPA. Factor analysis suggests that the combination of PAH compounds found in all site samples indicate a mixture of vehicular and combustion activities.**

Keywords **-** ***Polycyclic Aromatic Hydrocarbon, Semi Arid Region, Particulate Pollution, Toxic Equivalent Factor***

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds constituting only carbon and hydrogen, arranged in two or more aromatic rings. They are ubiquitous contaminants of great environmental concern and are "primary condensates", formed from both natural and anthropogenic sources, with the latter being now by far the major contributors. Natural sources include combustion (forest fires and volcanos) and biosynthesis (sediment diagenesis, tar pits and biological conversion of biogenic precursors) Anthropogenic sources are the major contributors of the more hazardous PAH species and include "mobile" sources and "stationary" categories. Mobile categories are mainly vehicular (petrol and diesel engines) and tobacco smoking. Stationary categories include domestic heating, refuse burning and industrial activities such as metallurgical enterprises, foundries, timber treatment plants, as well as industries focusing on the carbonisation, distillation and gasification of coal (for example, coke plants and manufacture of creosote).

Both natural and anthropogenic sources give rise to PAH formation by means of the incomplete combustion of organic materials containing carbon and hydrogen. Combustion-generated PAH are initially generated at source in the gaseous state, a proportion of which then adsorb onto existing particles upon cooling of the emission. At the higher temperatures of combustion sources, larger proportions are present in the vapour phase. Sixteen unsubstituted PAHs, some of which are considered as being possible or probable human carcinogens, have been listed by the US Environmental Protection Agency (EPA) as priority pollutants. Once they enter the atmosphere, PAHs are partitioned between the particulate matter and gas phases, depending on the PAH molecular weight. Low molecular weight PAHs has higher concentrations in the vapor phase while high molecular weight PAHs is often associated with particles. Polycyclic aromatic compounds (PAC) comprise the largest single class of suspected chemical carcinogens currently known to man. Before industrialisation a natural balance existed between the production and natural degradation of PAC, which kept the background concentration low and fixed. However, this natural balance has been disturbed with increased development throughout the world. Due to their potential mutagenicity and carcinogenicity, many regulations on PAH emissions have been proposed. A maximum permissible risk level of 1 ng/m^3 benzo[a] pyrene (BaP) in ambient air, based on the carcinogenic potential of inhaled particulate PAHs is reported. To the best of our knowledge, however, the environmental health risk associated with exposure to atmospheric particulate PAHs has yet to be assessed for India. There is a general lack of standardized methods employed for the sampling and analysis of PAH .

In India, few studies have examined atmospheric PAH concentrations in Delhi, Mumbai, or Ahmedabad. Therefore, in continuation of our earlier studies on PAH [1], this present study ascertained PAH concentrations in ambient air at Agra, a semi-arid region of India, and identified sources based on variations in PAH profiles and land use among the sites. The study also assessed the carcinogenic potency of PAHs at each location.

II. METHODS & MATERIALS

A. Site Description

Agra, the city of Taj (27°10'N 78°02'E) is situated on the West bank of river Yamuna in the north central part of India about 200 kilometers (km) south of Delhi in the Indian state of Uttar Pradesh. As the home of the Taj Mahal, Agra is one of the most famous tourist spots in the world. Agra city is considered to be a semi-arid zone as two-thirds of its boundaries are surrounded by the Thar Desert of Rajasthan. Summer season comprises of four months i.e. from March to June. During the sampling period the temperature and relative humidity ranges from 15.4°C to 48.8°C and 18.4%-62.7% respectively. The down ward wind is west and north-north-west and its speed ranges from 0.2 m s^{-1} to 9.2 m s^{-1} in summers. In Agra, 60% pollution is due to vehicular emission.The atmospheric pollution load is high and because of the down ward wind, pollutants may be transported to the different areas mainly from an oil refinery situated in Mathura (50 kms from the centre of Agra City). This period is often characterized by strong dust storms caused due to low pressure developed in this area. **Figure 1** is showing different cites in the city map of Agra.

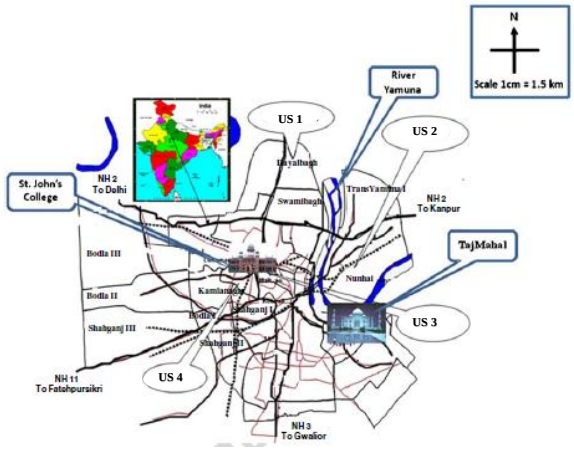

Fig. 1: Map of Agra showing different cites

B. Air Sampling

Air sampling stations were set up in the four previously described locations. Each station was monitored for ambient air quality twice a month in a scheduled manner. Particulate Matter (PM_{10}) in air were collected on 20.3 x 25.4 cm^2 glass fiber filter paper (EPM-2000) using respirable dust samplers (RSPM Envirotech Sampler RDS, 460 DX, New Delhi, India) at the rate of 1.0 cubic meter per minute (m^3/min). The air suction rate was verified every week using calibrated rotameters with an accuracy of ±1%. Lot blanks and TSP filter paper samples were kept in desiccators overnight and were weighed on a microbalance accurate to 0.1 milligrams (mg). Samples were stored in a cool, dark place until analysis.

C. Extraction and Analysis

The Samples and blanks were extracted with 140 milliliters (mL) methylene chloride by Soxtherm®. Blank spike/blank spike duplicate (BS/BSD) samples (spiked with PAH spiking solution) were extracted using clean fibreglass thimbles. No surrogates were added. After the samples were extracted for one programmed cycle, 100 mL of additional solvent was added. All samples were extracted for another programmed cycle and then concentrated to 1.0 mL. Internal standards were added to all extracts prior to sample injection. The gas chromatograph (GC) oven was temperature programmed to separate the method analytes on a fused silica column, which were then detected with a mass spectrometer (MS). Analyses were conducted according to the procedures listed in Response Engineering and Analytical Contract, USEPA, Standard Operating Procedure [2]. The REAC method is based on modified National Institute for Occupational Safety and Health (NIOSH) Method 5515 for the analysis of PAHs in air samples [3].Internal standard areas were all within quality control (QC) criteria. BS/BSD % recoveries ranged from 61% to 80%. All relative percent differences (RPDs) were between 3% and 6%. Identification was accomplished by comparing the retention times and mass spectral data of the sample target compounds to the standards. Quantification of PAH compounds was accomplished using the internal standard method. The area of the primary characteristic ions (i.e., d8-Naphthalene, d10-Acenaphthene, d10-Phenanthrene, d12-Chrysene and d12-Perylene) were used to quantify the PAH target compound in the samples.

III. RESULTS & DISCUSSION

D. PAH in air particles

Figure 2 shows the variation in the concentration of individual PAHs depending on different locations. The TPAH concentrations were 76.6, 27.9, 23.7 and 6.5 ng m^{-3} at industrial, residential, roadside, and agricultural sites, respectively. The combined mean concentration of TPAH was 33.7 ng m^{-3} for all sites.

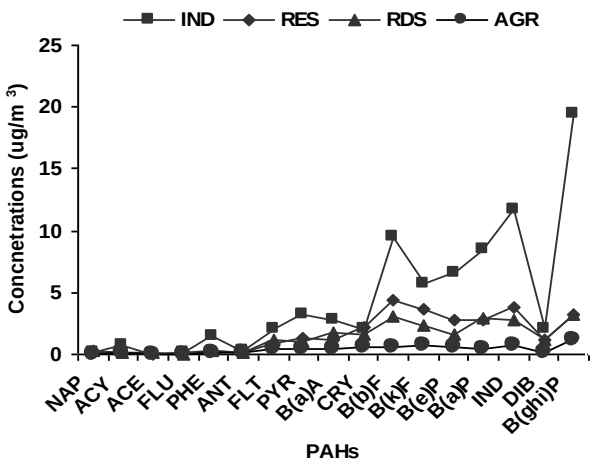

Fig 2: Concentration of individual PAHs at different locations

The industrial site had the highest TPAH concentration followed by the residential, roadside and agricultural sites. These results also indicate that PAH concentrations are strongly linked to land use.

Figure 3 shows the relative contribution of 2-, 3-, 4-, 5-, and 6-ring PAHs in the atmosphere at the locations investigated in this study.

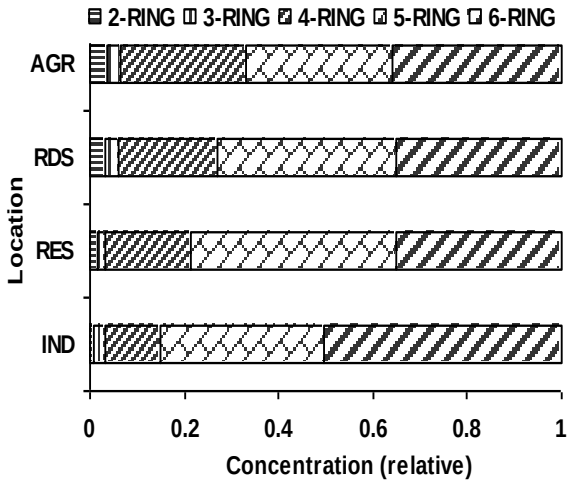

Fig. 3: Relative contribution of 2, 3, 4, 5 and 6-ring PAHs at different sites

The average TPAH percentage based on the number of rings were 1.6% (2-ring), 2.4% (3-ring), 15.3% (4-ring), 36.7% (5- ring), and 44.0% (6-ring) as shown in Figure 4.

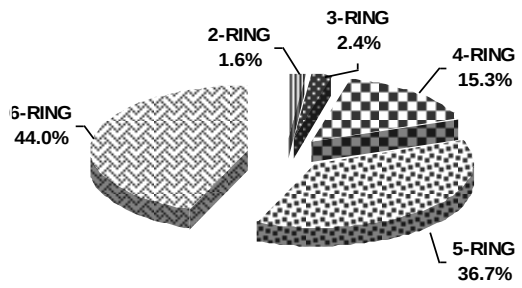

Fig. 4: Average TPAHs percentage at Agra

The concentration trends of the major PAH found in this study were: benzo (g, h, i)perylene > indeno(123-cd)pyrene > benzo(b)fluoranthene > benzo(a)pyrene at the industrial site; benzo(b)fluoranthene > indeno(123-cd)pyrene > benzo(k)fluoranthene > benzo(g,h,i)perylene at the residential site; benzo(g,h,i)perylene > benzo(b)fluoranthene > benzo(a)pyrene > indeno(123-cd)pyrene at the roadside site: and benzo(g,h,i)perylene > indeno(123-cd)pyrene > benzo(k)fluoranthene > benzo(b)fluoranthene at the agricultural site. At all the sites, indeno(123-cd)pyrene, benzo(g,h,i)perylene, and benzo(b)fluoranthene were the predominant compounds.

E. Factor Analysis

A varimax rotated factor analysis was performed to identify the main sources influencing the PAH concentration at the sampling sites. The varimax procedure was adopted for rotation of the factor matrix to transfer the initial matrix into one that was easier to interpret. In the present study, the SPSS (version 10.0) computer software was used to perform factor analysis. Results obtained by varimax rotated factor analysis are given in **Table 1**.

TABLE I: RESULTS OF FACTOR ANALYSIS WITH VARIMAX ROTATION ON PAHS IN AIR AT INDUSTRIAL, RESIDENTIAL AND ROADSIDE SITES OF AGRA

PAHs	Industrial	Residential	Roadside
	Factor 1	Factor 1	Factor 1
NAP	0.75	0.89	0.96
ACY	-	0.95	0.83
ACE+FLU	0.77	0.91	0.96
PHE	0.84	0.87	0.97
ANT	0.96		0.85
FLT	0.65	0.92	0.94
PYR	0.87	-	0.59
B(a)A	0.94	0.94	0.91
CHR	0.78	0.69	0.93
B(b)F	0.87	0.71	0.98
B(k)F	0.75	-	0.91
B(a)P	-	-	0.63
B(ghi)P	0.89	0.98	0.89
Eigen Value	8.8	8.6	9.7
% of Variance	83.4	89.7	87.6
Cumulative %	83.4	89.7	87.6
Predicted Sources	Oil combustion activities	Oil burning and incineration	Vehicular activities

Loading greater than 0.5 is significant

Shown results in the table have loading > 0.5, because they are deemed to be statistically significant. As presented in Table 1, at the entire sites only one factor is extracted except that of agricultural site which is having two factors. Industrial, residential and roadside contributed 83.4%, 89.7%, 87.6%, variance of data set, respectively, whereas Table 2 shows that at the agricultural site total of 98.4% data is extracted with the two factors, 74.8% and 23.6% loading of each group. As from Table 1, in industrial area, coal burning and oil combustion may be the major source of PAH's as they are used for heating the furnaces etc. Similarly, in residential areas incineration as well as diesel burning might be the source of air PAH. Diesel generators are used to generate electricity because of erratic supply of electricity in the residential areas. Whereas in roadside area, the main source of PAH are vehicular activities. Number of the diesel and petrol vehicles especially two and three wheelers is used for local transportation of the public (traffic density is about 105vehicles per day). As in Table 2, agricultural areas having two factors suggests that the burning of wood, cow-dung cakes, coal and incineration may be the potential sources of PAH in air, as all wastes are dumped out of the city which are very close to these agricultural sites and this dumped waste is incinerated time to time. Moreover, pumping sets is also used for the irrigation purpose, which is run by diesel. In above all, Mathura refinery is situated at about 40 km of the Agra city. The unit must be emit significant amount of the PAH's which can probably get transported to the Agra city.

TABLE III: RESULTS OF FACTOR ANALYSIS WITH VARIMAX ROTATION ON PAHS IN AIR AT AGRICULTURAL SITE OF AGRA

PAHs	Agricultural	
	Factor 1	Factor 2
NAP	0.71	0.51
ACY	0.83	0.74
ACE+FLU	-	-
PHE	0.19	0.67
ANT	0.97	0.59
FLT	0.91	0.61
PYR	0.67	0.73
B(a)A	0.66	0.97
CHR	0.89	0.58
B(b)F	0.97	0.65
B(k)F	-	0.66
B(a)P	-	-
B(ghi)P	0.79	0.90
Eigen Value	7.1	6.7
% of Variance	74.8	23.6
Cumulative %	74.8	98.4
Predicted Sources	Cow dung/wood/coal combustion	Incineration

Loading greater than 0.5 is significant

Thus, obtained results of factor analysis suggest that the mixed signature of all the sources are intermediate between vehicular and combustion activities.

F. Assessing PAH exposure profiles

According to International Agency for Research on Cancer (IARC, 1987), benzo(a)pyrene is the most carcinogenic compound and it is classified into probable (2A) or possible (2B) human carcinogens. BaP is a five ring ($C_{20}H_{12}$) compound, which is mutagenic for human cells in culture [4] and carcinogenic in whole animal assays [5]. The toxic equivalent factor for BaP is one (1), which is highest among all the PAHs [6]. One approach in estimating the carcinogenic potency associated with the exposure of a given PAH compound can be obtained by calculating its BaP_{eq} for each individual PAH species. In order to calculate the carcinogenic potencies associated with the total PAH exposures from air; we pragmatically used the sum of each individual BaPeq (i.e., total-BaP_{eq}) as a surrogate indicator. Therefore in the present study toxic equivalent factor (TEF) of the given species relative to BaP carcinogenic potency have been used. For pragmatic purpose, the list of TEFs compiled by Tsai et al. [7] was adopted in this study. Table 3 indicates the mean concentration of TPAHs in Agra to be 33.7 ng m^{-3}, which corresponds to a B(a)P equivalent exposure of 6.1 ng m^{-3}.

TABLE III: BAP TOXIC EQUIVALENCY FACTORS (TEFS) AND BAP_{EQ} EXPOSURE PROFILES (NG M^{-3})

PAHs	MEAN	*TEFs	$BaP_{exposure}$
NAP	0.15	0.001	0.00015
ACY	0.28	0.001	0.00028
ACE	0.05	0.001	0.00005
FLU	0.08	0.001	0.00008
PHE	0.55	0.001	0.00055
ANT	0.18	0.01	0.0018
FLT	1.15	0.001	0.00115
PYR	1.54	0.001	0.00154
BAA	1.53	0.1	0.00153
CHR	1.60	0.01	0.160
BBF	4.36	0.1	0.0436
BKF	3.11	0.1	0.311
B(e)P	2.89	0.1	0.289
B(a)P	3.66	1	3.66
I(123cd)P	4.71	0.1	0.471
D(ah)A	1.13	1	1.13
B(ghi)P	6.74	0.01	0.0674
TOTAL	**33.7**		**6.1**

*TEFs cited by Tsai et al. (2004)

IV. CONCLUSION

A total of 17 PAH compounds were found in the atmospheric particles of Agra during summers. The TPAH concentrations were found to be 76.6, 27.9, 23.7 and 6.5 ng m^{-3} at industrial, residential, roadside and agricultural sites, respectively. The combined mean concentration of TPAH was 33.7 ng m^{-3} for all sites. At all the sites, indeno(123-cd)pyrene, benzo(g,h,i)perylene, and benzo(b)fluoranthene were the predominant compounds as a result of anthropogenic activities. The industrial sites had the highest TPAH concentration followed by the residential, roadside and agricultural sites. The average percentage of TPAH was 0.67%, 3.41%, 21.72%, 41.18%, and 33.05% for 2-, 3-, 4-, 5- and 6-ring compounds respectively. Using a Toxic Equivalent Factors approach, the mean concentration of TPAH corresponds to about 6.1 ng m^{-3} of B(a)P with respect to carcinogenic potency.

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